Derivation-Based pH Correction Method for High-Weight Salt-Saturated Water-Based Mud (SSWBM)

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Abstract

Accurate pH measurement in High-Weight, Salt Saturated Water-Based Mud (>20 kPa/m) is frequently compromised by extreme salinity and high solids content, which interfere with conventional measurement techniques, presenting significant technical challenges at rig sites, in high-pressure salt formation sections in the Middle East. Extreme salinity typical of regional deep well operation (approximately 190 kg/m3) masks pH paper response, while high barite solids (~ 40%) rapidly coat pH meter electrodes, resulting in falsely low pH readings. This paper presents a pH correction framework based on fundamental dilution principles and logarithmic relationships between ion concentration and pH. The theoretical approach is supported by laboratory datasets. A 1:1 dilution combined with a +0.3 correction factor is proposed for practical field application. This framework is suitable for technical discussion and future experimental validation.

Keywords: pH Measurement; Salt Saturated Water-Based Mud (SSWBM); High Weight Drilling Fluids, Dilution Factor; pH Correction

1. Introduction

pH is a critical control parameter in water-based drilling fluids, influencing corrosion control, chemical efficiency, polymer stability, and overall mud behavior. In high-weight salt-saturated systems, direct pH measurement is often unreliable due to salinity and solids interference.

2. Problem Statement

Direct pH measurements in High-Weight SSWBM are persistently inaccurate and underestimated due to chloride masking and electrode coating. Inaccurate pH values can mislead troubleshooting related to polymer degradation, rheology variation, contamination, and well control gas interpretation.

3. Theoretical Framework

The proposed methodology relies on the relationship between ion concentration and the logarithmic pH Scale

3.1 Fundamental pH Relationships

The pH of an aqueous solution is defined as the negative logarithm of hydrogen ion concentration:

$pH = -\log[H^+]$

For basic systems, hydroxyl ion concentration is expressed as:

$pOH = -\log [OH^-]$

H^+ and OH^- are always present in aqueous solution in equilibrium expression. At a temperature of 25 °C, this relationship is expressed as

$pH + pOH = 14$ (25 °C)

3.2 Dilution Theory

Dilution is defined as the reduction of solute (ions) concentration by the addition of solvent (distilled water) without changing the total number of moles of solute. The governing mass-balance equation is:

$C_1V_1 = C_2V_2$,

where C is ion concentration and V is solution volume. Subscripts 1 and 2 refers to the conditions before and after dilution, respectively.

The dilution factor (f) is defined as the ratio of final volume to initial volume:

$$f = V_2 / V_1$$

For a dilution ratio of 1: n by volume, where n represents the number of parts of water added to one part of sample:

$$f = \frac{1+n}{1} = 1+n$$

Accordingly, the ion concentration after dilution becomes:

$$C_2 = C_1 / f$$

4. Derivation of the pH Correction Equation

A generalized logarithmic concentration term can be defined for any ionic species:

$$PC_2: = -\log(C_2)$$

After dilution, this term becomes:

$$pC_2 = -\log(\frac{C_1}{f})$$

$$pC_2 = -(\log C_1 - \log f)$$

$$\mathbf{pC_2 = -\log C_1 + \log f}$$

This expression forms the basis for pH correction in both acidic and basic systems.

4.1 For Acidic Media (H^+ dominant)

$pH = -\log (H^+)$

After dilution:

$pH_2 = -\log (H_1^+) + \log f$

Compensating, $PH_1 = -\log (H_1^+)$

$pH_2 = PH_1 + \log f$

Rearrange the equation

$pH_1 = PH_2 - \log f$

$$\mathbf{pH_{Original} = pH_{diluted} - \log f}$$

4.2 For Basic Media (OH^{-}dominant)

pOH = - log (OH^{-})

After dilution:

pOH_2= - log (OH_1^{-}) + log f

Compensating, pOH_1 = - log (OH_1^{-})

pOH_2 = pOH_1 + log f

Using the relationship, pOH = 14 – pH:

14-pH_2 = pOH_1 + log f

pH_2 = 14 - (pOH_1 + log f)

pH_2 = (14-pOH_1) - log f

Compensating, pH_1 = 14-pOH_1

pH_2 = pH_1 - log f

Rearrange the equation

pH_1= PH_2 + log f

$\mathbf{pH_{original} = pH_{Diluted} + \log f}$

5. Experimental Observation of Dilution Effects on Alkaline pH Measurement

5.1 Factors Influencing pH in Diluted Samples

While the correction framework is derived from dilution theory, a laboratory observation was conducted to examine how dilution influences measured pH in alkaline solutions.

pH electrodes measure hydrogen ion activity ($a\,\mathbf{H}^{+}$) rather than concentration [$\mathbf{H}^{+}$]. The relationship is defined as a $\mathbf{H}^{+}$ = γ. [$\mathbf{H}^{+}$], where γ represents the activity coefficient.

When dilution occurs, the following physical changes take place:

- **Concentration Reduction**: The actual molar concentration of ions decreases.
- **Ionic Strength Change**: Dilution lowers the ionic strength (*I*) of the solution.
- **Activity Coefficient Shift**: These changes increase the activity coefficient γ, which can cause deviations between theoretical and measured pH values.
- **Buffering and Environmental Factors**: Dilution reduces buffering capacity and increases sensitivity to atmospheric CO2 absorption. Dissolved carbon dioxide forms carbonic acid, which consumes hydroxide ions and reduces Ph

5.2 Laboratory Dilution Study

A study was performed using sodium hydroxide (NaOH) solutions prepared in fresh water. The original solutions ($\mathbf{pH_0}$) were measured and then diluted with distilled water at specific ratios:

- **1:1 Ratio**: 25 ml Solution + 25 ml distilled water.
- **1:2 Ratio**: 25 ml Solution + 50 ml distilled water.
- **1:3 Ratio**: 25 ml Solution + 75 ml distilled water.

The measured change in pH (ΔpH) was compared against theoretical logarithmic factors:

- **ΔpH1** (1:1 dilution) meets the theoretical **log2** factor (0.30).
- **ΔpH2** (1:2 dilution) meets the theoretical **log3** factor (0.48).
- **ΔpH3** (1:3 dilution) meets the theoretical **log4** factor (0.60).

5.3 Experimental Data

NaOH	**pH_0**	**pH_1 (1:**	**pH_2 (1:**	**pH_3 (1:**	**ΔpH**	**ΔpH**	**ΔpH**
2.00	12.47	12.27	12.12	12.01	0.20	0.35	0.46
1.80	12.43	12.20	12.05	11.91	0.23	0.38	0.52
1.60	12.40	12.19	12.00	11.85	0.21	0.40	0.55
1.40	12.36	12.10	11.92	11.73	0.26	0.44	0.63
1.20	12.25	11.99	11.77	11.54	0.26	0.48	0.71
1.00	12.09	11.85	11.61	11.38	0.24	0.48	0.71
0.80	11.90	11.60	11.38	11.14	0.30	0.52	0.76
0.60	11.63	11.24	10.94	10.54	0.39	0.69	1.09
0.50	11.33	10.95	10.66	10.37	0.38	0.67	0.96
0.40	11.24	10.96	10.68	10.43	0.28	0.56	0.81
0.30	11.05	10.77	10.41	10.18	0.28	0.64	0.87
0.20	10.87	10.48	10.21	10.03	0.39	0.66	0.84
0.10	10.33	9.99	9.54	9.29	0.34	0.79	1.04
0.09	10.31	9.98	9.76	9.62	0.33	0.55	0.69
0.08	9.89	9.62	9.42	9.25	0.27	0.47	0.64
0.07	9.63	9.30	9.15	8.96	0.33	0.48	0.67
0.05	9.50	9.19	9.01	8.98	0.31	0.49	0.52
0.03	9.16	8.74	8.45	8.12	0.42	0.71	1.04
0.01	8.63	8.20	7.96	7.86	0.43	0.67	0.77

5.4 Observed Trends and analysis

The experimental data revealed distinct behaviors across different pH ranges:

- **At very high alkalinity (pH > 12.4),** the observed dilution effect is smaller than theoretical predictions because ionic strength remains high and the system is strongly buffered.
- **Intermediate Range (pH 12.0 – 12.36)**, measured dilution corrections are slightly lower than theoretical values at low and medium dilution ratios but begin to exceed theoretical predictions at higher dilution levels.

- **Intermediate Range (pH 10.33 – 11.9)**, the dilution correction is close to theoretical predictions at the 1:1 dilution ratio. However, deviations begin to appear at medium and higher dilution ratios (1:2 and 1:3), indicating increasing the influences of Coefficient activity. In "ionic crowded" media, small reductions in the activity coefficient cause higher deviations in the pH reading.
- **Operating Range (pH 9.5 – 10.31)**: This range corresponds to the typical operating pH of drilling fluids. Measured results closely match theoretical dilution predictions across all tested ratios, reflecting maximum stability and logical alignment with logarithmic corrections.
- **Lower pH Values (pH 8.63 – 9.16)**: Deviations become significant due to reduced buffer capacity and the stronger influence of atmospheric CO2.

6. Engineering Interpretation

The dilution ratio 1:1 reduces chloride concentration and total solids allowing more contact between pH reader and aqueous phase resulting in accurate pH record

The correction (Log 2) restores the original pH by compensating for dilution-induced concentration reduction without altering acid–base equilibrium.

7. Assumptions and Limitations

Ideal dilution and constant temperature are assumed. The method is intended for engineering estimation rather than analytical precision.

8. Recommended Field Procedures

A 1:1 Ratio is sufficient for accurate recording in the field

Sample Type	Sample Vol.	Distilled Water	Equipment	Correction **(Log 2)**
Filtrate	5 ml	5 ml	pH Strips	Add 0.3
Mud	25 ml	25 ml	pH Meter	Add 0.3

- Collect the sample (filtrate or mud)
- Add an equal volume of distilled water
- Stir thoroughly (rod for filtrate; magnetic stirrer for mud)
- Measure the pH and add 0.3 correction factor to the result
- Note: pH strips must be high sensitivity to observe the difference

9. Conclusion

A derivation-based pH correction framework for high-weight SSWBM systems has been presented, providing a transparent and honest approach for addressing measurement challenges.

Since, the medium of WBM is basic, the pH correction is governed by the equation $\mathrm{pH}_{\mathrm{original}} = \mathrm{pH}_{\mathrm{Diluted}} + \log f$

The application of a 0.3 correction factor to 1:1 diluted sample effectively bypasses the masking and coating effects of High weight SSWBM. This ensures that mud engineers can accurately measure mud pH and eliminate uncertainty in pH reading, enabling them to troubleshoot mud problems correctly without the influence of pH in accuracies.

10. Future Experimental Validation

Future laboratory and field testing are recommended. Controlled laboratory tests using salt-saturated, high-weight water-based mud systems can be conducted to compare direct pH measurements with diluted and corrected values over a range of salinity levels, solids concentrations, and alkalinity conditions. Field trials under actual drilling conditions would further support the strength of the methodology by evaluating repeatability and operational practicality.

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